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Exciplex Formation Between Silver Ions and the Lowest MLCT Excited
State of the Tris(Bipyrazine)Ruthenium(II) Cation

By

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in

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Exciplex Formation Between Silver Ions and the Lowest MLCT Excited State of the Tris(Bipyrazine)Ruthenium(II) Cation

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Abstract

The lowest excited MLCT state of the $[Ru(bpz)_3]^{2+}$ cation, **1**, is shown to react with silver ion in aqueous or acetonitrile solution to form exciplexes with up to six silver ions per excited cation. Lifetime, wavelength data are presented as a function of the [Ag]/[Ru] ratio. An excited state (reductive quenching) potential of 1.55V is derived from quenching by a range of methoxybenzenes. Data for quenching by metal ions are also presented. There is no ground state interaction between **1** and silver ions.

The $[Ru(bpz)_3]^{2+}$ ion (**1**) (bpz = 2,2'-bipyrazine) has been the subject of extensive investigation [1-18] because of its utility as a photo- catalyst and its complementarity to the $[Ru(bpy)_3]^{2+}$ ion (**2**) (bpy = 2,2'-bipyridine)[19]. A characteristic of **1**, not shared by **2**, is the presence of six peripheral nitrogen atoms each with a lone pair of electrons capable of donation to a Lewis acid [20]. Thus, ground state

1, and related bipyrazine complexes, have been observed to coordinate with protons [14,20], pentacyanoferrate(II),[5], boron trifluoride [20], and pentammineruthenium(II)/(III) [21]. During a recent study of the luminescence quenching of 1, it was observed that silver ions did not quench the lowest excited metal to ligand charge transfer (MLCT) transition while many organic quenchers and other metal ions were effective [8]. By analogy with the quenching behaviour of 2 [19], this was an unexpected result. However Kobayashi and co-workers have briefly reported reaction of silver ions with the peripheral nitrogen atoms of the [Ru(bpy)2(bpz)]$^{2+}$ cation [22]. A ruthenium tris(bipyrazine) excited state cation with six silver atoms bound to the peripheral nitrogen atoms would possess a formal charge of 8+ and would thereby be expected to be a much stronger excited state oxidant than 1 itself, and conceivably strong enough to oxidise water directly, providing a good rationale for the study.

Experimental

Materials: Ru(bpz)3(PF6)2 was synthesized and purified as previously described [17]. AgNO3, KNO3, Cu(NO3)2.6H2O and Ni(NO3)2.6H2O were analytical grade. A loan of RuCl3.3H2O from Johnson Matthey is gratefully acknowledged. The series of methoxybenzenes was used without further purification. Aqueous solutions were prepared with water which had been doubly distilled from KMnO4 and passed through both mixed bed and organic water purification cartridges (Barnstead). Acetonitrile was Aldrich Gold Label. Tetrabutylammonium perchlorate (Eastman) (TBAP) was recrystallized from ethanol and vacuum dried.

Luminescent emission measurements: Emission spectra were recorded with a Varian SF-330 spectrofluorimeter.   The exciting wavelength was 423 nm. In both solvent systems, the concentration of $[Ru(bpz)_3]^{2+}$ was about 1.6 x 10^{-5}M. Solutions were prepared in 0.1M KNO_3 or 0.01M TBAP in CH_3CN to maintain constant ionic strength. In both systems, the PF_6^- salt of the ruthenium complex was used to eliminate possible formation of AgCl.

The methodology of obtaining the luminescence measurements was the same as reported previously [8], and emission intensities were corrected for the inner filter effect in the same manner as before. Quencher concentrations   were   in   the   range   of   0.01M - 0.1M for the methoxybenzenes, and 0.01M - 0.5M for the inorganic metal salts.

Lifetime measurements were carried out using a York University constructed 0.5MW pulsed nitrogen laser and a Princeton Applied Research (PARC) Model 162 boxcar averager with Model 165 and 166 gated integrators.   Data were plotted on a X-Y recorder and lifetimes calculated by manual transfer of the data to an appropriate computer program. All solutions were nitrogen outgassed before study.

Other measurements: Absorption spectra were recorded on a Perkin-Elmer Hitachi Model 340 microprocessor spectrometer. ^{1}H NMR spectra were recorded in D_2O with a Bruker Aspect 300 spectrometer. Chemical shifts and scale are reported downfield from DSS. FTIR spectra were recorded as KBr discs using a Nicolet SX20 spectrometer.

Results

i) <u>Ground state studies;</u> The addition of silver ion, as AgClO4 or AgNO3, to aqueous solutions of <u>1</u> in 0-1500:1 molar ratio, and in the presence of 0.1M or 0.01M KNO3 causes no change in the electronic absorption (visible or ultra-violet region) spectrum of <u>1</u>. Moreover the ^{1}H NMR spectrum of <u>1</u> in water is unperturbed by the addition of excess silver ion. In another experiment, [Ru(bpz)3](ClO4)2 and excess AgClO4 were heated in water for 3 hr and then evaporated to dryness. The FTIR spectrum of the resulting solid was indistinguishable from that of a physical mixture of the reactants.

ii) <u>Excited state studies</u>; a) **Wavelength dependence:-** When excited at 450 nm into the allowed lowest singlet-singlet MLCT transition, complex <u>1</u> emits near 600 nm from the [3]MLCT state (1*) associated with the $Ru(t_{2g})^6$ ------> $\pi^*(1)$ (bpz) transition (Fig.1) [17]. The wavelength of this emission depends upon added silver ion, shifting to the red (in aqueous or acetonitrile solution) (Fig.2) as the [Ag]/[Ru] molar ratio increases. The emission wavelength approaches a limiting value at molar ratios exceeding 10000:1. The shift is most dramatic at ratios of 100-1000, with no shift within experimental error below 100:1 ratio. The shift, in water, is about 2nm larger in 0.1M KNO3 than in 0.01M KNO3.

b) **Lifetime measurements:-** The lifetimes (Fig.3) increase in acetonitrile and decrease in water with increasing [Ag]/[Ru] ratio.. The following empirical relationships pertain between lifetime (τ), in ns, and the [Ag]/[Ru] molar ratio:-

(CH3CN/0.01M TBAP) τ = 900 + 0.03 [Ag]/[Ru]   (R = 0.985)

(Water/0.1M KNO3) τ = 1060 - 0.013 [Ag]/[Ru]   (R = 0.947)   (1)

   A linear function is used for convenience to enable calculation of lifetimes at differing [Ag]/[Ru] ratio. However the correlation

coefficients are not so good as to exclude a more complex dependence.

iii) Quenching studies:; The quenching of 1* with various organic acceptors and donors in acetonitrile, and with metal ions in water, has been previously reported [8]. These studies are extended here through re-investigation in the presence of varying amounts of Ag$^+$ ion. In Fig.4, and Table 1, are shown Stern-Volmer slopes [24], Ksv, for a variety of organic donors versus the [Ag]/[Ru] ratio, and the $E(Q^+/Q)$ potential. Quenching data for various metal ions in aqueous solution are also presented in Table 1. NB All the above data are collected in nitrogen outgassed solutions. Oxygen is a fairly effective quencher.

Discussion

The uv/vis/ir and especially nmr data show no detectable interaction between the ground state of 1 and silver ions under the conditions explored. The shift in wavelength of the emission from 1*, and the increase in lifetime observed in acetonitrile solution show conclusively the interaction of silver ions with the lowest MLCT state of complex 1, i.e. exciplexes are formed. The variation in lifetime and quenching Ksv values with [Ag]/[Ru] ratio provides evidence for a series of 1(Ag$_n$)* exciplexes, apparently in equilibrium with each other and with the silver ion. The possibility that the shift in peak emission wavelength maxima occurs through solvent dielectric changes is reduced by the use of constant ionic strength solutions, at least at lower [Ag]/[Ru] ratios. At high [Ag]/[Ru] ratios, the silver ion concentration exceeds that of TBAP and may therefore introduce solvent dielectric effects. However at these high [Ag]/[Ru] ratios, the increase in emission wavelength has essentially leveled off. To increase the TBAP concentration is not practical due to precipitation of (1).

It does not appear possible from the data available to determine the values of n. The simplest explanation is that one silver atom is bound readily in the [Ag]/[Ru] = 100 - 2000:1 range, and that a second binds with difficulty in the 2000 - 10000:1 range. However the data do not distinguish an alternative explanation, namely, that in a manner similar to protonation [14], three silver atoms bind in the lower [Ag]/[Ru] range one on each bipyrazine ring, and that 4-6 silver atoms bind in the higher [Ag]/[Ru] range. Given the increased shifts in emission wavelength for given [Ag]/[Ru], with increasing ionic strength, multiple silver ion binding is inferred. For the purposes of discussion, therefore, the latter possibility will be assumed.

The red shift in the emission maximum reflects the Lewis acidity of the Ag^+ ions which stabilise slightly the π^* levels involved in the MLCT transition. Note that this red shift is in contrast to the unexpected blue shift observed when silver ions bind the peripheral nitrogen atoms of the $[Ru(bpy)_2(bpz)]^{2+}$ cation [24]. The extended lifetime of the silver bound excited states in acetonitrile solution may reflect reduced solvent collisional deactivation of the excited state whose wave function may not extend significantly over the silver ions.

The ^{3}MLCT excited 1* cation is an excellent oxidising agent with a potential of +1.45V for the couple $[Ru(bpz)_3^{2+*}]/[Ru(bpz)_3^+]$, being about 0.7V more positive than for the corresponding couple for 2* [8]. The excited state potential of the species $[Ru(bpz)_3Ag_n]^{2+n*}$ can be determined via quenching studies (restricted by the requirement that the quencher does not react with silver ion, eliminating, for example, quenching by aromatic amines and nitro derivatives).

The (reductive) quenching data for a range of alkoxybenzenes do indeed reflect the increased oxidising ability of the 1(Ag$_n$)* system

when compared to 1* in the absence of silver (Table 1). The Ksv   values increase with decreasing E(Q+/Q) and increasing [Ag]/[Ru] ratio (Fig.4, Table 1). However we note that if the Ksv values are corrected for the variation in lifetime (via equation (1)), then the resulting kq values (Table 1) tend to be independent of the [Ag]/[Ru] ratio above about 2000:1.

Applying the Rehm-Weller theory [2ʒ] to the data as discussed previously [8], and assuming that the encounter volume and diffusion rate constants remain unchanged (a pragmatic assumption given the rather limited accuracy of this type of experiment) the data (for high [Ag]/[Ru] ratio) may be fitted with an excited state reduction potential of about 1.55V, or about 100mV more positive than for 1* alone.   The data are not good enough to delineate any special dependence upon n. Given that there is also a shift of about 100mV to the red, in the emission energy at high [Ag]/[Ru] ratio, the silver ions and the increased positive charge they impose, have actually increased the oxidising power of 1* by about 200mV, half of which is wasted.

Table 1 also includes data for quenching by metal ions in aqueous solution.   Indeed the species may be a better oxidising agent in aqueous solution than in acetonitrile wherein the (formal) 8+ charge is probably largely vitiated by ion pairing. However, in contrast to the acetonitrile data, the trends in the metal quenching data are for a reduction of Ksv, and kq, with increasing [Ag]/[Ru] irrespective of whether the metal ion is a reductive quencher such as Fe^{2+} or an oxidative quencher such as [Co(NH$_3$)$_5$Cl]$^{2+}$, or perhaps Cu^{2+}. This trend is seen most readily in the Cu^{2+} and Ni^{2+} data shown in Table 1.

The dominant factor in this aqueous metal ion quenching is the increasing positive charge of the excited state species, with increasing

[Ag]/[Ru], causing repulsion of these positively charged quenchers. Indeed this may be evidence that the number of silver ions bound to $\underline{1}^*$ does increase with increasing [Ag]/[Ru]. Note further that K_{SV} does increase with increasing ionic strength for a given [Ag]/[Ru] ratio.

Conclusions: The $[Ru(bpz)_3(Ag_n)]^{(2+n)+*}$ exciplexes are photocatalysts which should prove valuable for neutral or negatively charged quenchers which can tolerate excess silver ion. They also represent an interesting avenue for tuning the excited state potential of the $[Ru(bpz)_3]^{2+}$ photocatalyst.

Legends

Fig.1   Absorption and emission spectra of the $[Ru(bpz)_3]^{2+}$ cation in the absence of silver ion, and in the presence of silver nitrate at a molar ratio of [Ag]/[Ru] = 10000:1. The solution also contains 0.1M KNO_3.

Fig.2   Emission wavelength as a function of [Ag]/[Ru].
Lower data set (squares): Acetonitrile containing 0.01M TBAP. Upper data set (+): Water containing 0.1M KNO_3. Note the entry for 0 lies at 600nm. The slit width was 2nm, and the excitation wavelength 423nm.

Fig.3   Lifetime dependence as a function of [Ag]/[Ru].
a) Acetonitrile containing 0.01M TBAP. b) Water containing 0.1M KNO_3. Although a straight line is shown through these data, the correlation is not necessarily linear. Excitation wavelength 423nm.

Fig.4   Stern-Volmer slopes, Ksv as a function of quencher potential and [Ag]/[Ru] in acetonitrile (with 0.01M TBAP). The data are collected from a series of methoxybenzenes as listed in Table 1. From left to right on each line the [Ag]/[Ru] ratios are 0, 1000, 5000 and 10000.

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23. The Stern-Volmer slope is obtained from a plot of intensity of emission (I), as a function of quencher concentration [Q], with respect to the unquenched emission intensity I_o via:

$$I_o/I = 1 + K_{SV}[Q] = 1 + \gamma_o k_q [Q]$$

where γ_o is the lifetime of the excited state and k_q is the quenching rate constant.

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Table 1 Quenching Data in Acetonitrile and Water

Part I. Acetonitrile/0.01M TBAP[a]

[Ag]/[Ru]	124tmb	14dmb	12dmb	135tmb
10000	3625	1600	460	65
5000	3625	1400	370	60
1000	2860	1150	275	45
0	2145	635	125	20
$E(Q^+/Q)$[b]	1.12	1.34	1.45	1.49

a) 12dmb = 1,2-dimethoxybenzene; 14dmb = 1,4-dimethoxybenzene; 124tmb = 1,2,4-trimethoxybenzene; 135tmb = 1,3,5- trimethoxybenzene.

b) data in acetonitrile vs sce from A. Zweig, H.G. Hodgson, W.H.Jura. J. Am. Chem. Soc., 1964, 86, 4124.

Part II. Aqueous solution

Quencher	[KNO₃]	[Ag]/[Ru]	Ksv	$k_q{}^c \times 10^8$
$Fe^{2+}{}_{aq}$	1M	25000	540±80	7.3
		0		6[d]
$Co^{2+}{}_{aq}$	1M	10000	7	0.07
		1000	6±0.2	0.06
		0	17	0.16
$[Co(NH_3)_5Cl]^{2+}$	1M	10000	642	7
		0	620	5.8 (5.7)[d]
$Mn^{2+}{}_{aq}$	0.6M	12500	12±0.3[e]	0.13
$Cu^{2+}{}_{aq}$	1M	1000	486±1	4.6
		0	612±45	5.8 (5)[d]
	0.1M	3400	264±4	2.6
		0	330	3.1
$Ni^{2+}{}_{aq}$	1M	1000	178±5	1.7
		0	277	2.6
	0.1M	10000	53	0.6
		5000	95	1
		1000	165	1.6
		0	211	2

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c) Calculated from Ksv = $k_q t$ using lifetime equation in text.

d) Data for 1* in 1M KCl from ref.[8]

e) No quenching observed in the absence of silver ion.[8]

EMISSION AND ABSORPTION SPECTRA
$Ru(bpz)_3^{2+}/KNO_3$

Ag/Ru=0
λ_F=600nm →

Ag/Ru=10,000
λ_F=620nm →

Ag/Ru=0
AND
Ag/Ru=10,000

ABSORPTION

EMISSION

400   500   600   700

WAVELENGTH, nm

Y-axis: Lifetime ns. (Thousands)

X-axis: [AgI]/[Ru] (Thousands)

Legend: CH3CN □   Water ◇

Stern-Volmer slope, Ksv
(Thousands)

E(Q/Q+)